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Patterns of motion for random walkers under holonomic constraints

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Abstract. As models for polymer diffusion we consider the motion in two dimensions and three dimensions of four random walkers restricted by different holonomic constraints. The random walkers perform uncorrelated steps, which obey algebraic waiting-time distributions. We provide numerical results for the centre-of-mass motion and analytical approximations for the short- and long-time diffusion constants. Distinct from the two- and three-walkers problem we encounter here—depending on the constraints—partial nontrivial decoupling of the motion.

1. Introduction

Correlated motions of several random walkers occur in many physical problems. In previous works [1, 2] we have focused on sets of random walkers moving under holonomic constraints, a subject of much interest in polymer science; thus, according to the kink–jump model [3, 4] a macromolecular chain is described through N beads (random walkers) connected by $N-1$ rigid rods, where the beads move according to specific rules (i.e. 180° rotations of two neighbouring rods around the axis defined by the neighbouring beads and free orientations of the end beads). Our study is furthermore motivated by the diffusion of atomic clusters over surfaces and in the bulk [5–8]. We denote the waiting-time density (WTD) between consecutive steps of each bead by $\Psi(t)$.

If the WTD is exponential then the number of jumps $n(t)$ within a time interval $(0, t)$ is Poisson distributed [9, 10]. Transport in amorphous materials [11, 12] or reactions and relaxations in disordered media [13–16] often lead to more complex WTDs. Thus, in melts and dense solutions a kink–jump requires some free volume; this leads to the Glarum model [17] and continuous-time random walks (CTRW) [11, 15, 18]. Given that the free volume is provided by randomly moving vacancies, the WTD follows a power law [15, 18]. WTDs of this kind have already been used in order to describe polymer melts and concentrated solutions [19].

In previous works the motion of a dumbbell in one dimension [1] and that of an equilateral triangle in two dimensions [2] were considered. The dumbbell consists of two beads (random walkers) connected by a rigid segment and moves along a line through flips, such that one bead pauses and the other one jumps over it. By this the centre-of-mass (CM) of the dumbbell makes a step to the left (to the right) when the right (the left) bead moves, and the overall shape of the dumbbell is unchanged [1]. The two dimensional motion of an

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equilateral triangle (made of three random walkers, its vertices, and three rigid segments, its sides) according to the kink–jump model is similar: when one vertex moves, the triangle flips around the side whose two vertices are at rest. This corresponds to a reflection around this side; the triangle's shape is unchanged and its CM performs a random walk on a two-dimensional hexagonal lattice [2]. In both cases (dumbbell and triangle) the spatial and temporal aspects of the motion are strongly coupled [1, 2].

In this paper we analyse the dynamics of four random walkers under holonomic constraints. When four walkers are connected to make a ring (system Q) and move according to kink–jump rules, then the system can change (distinct from [1] and [2]) its shape. We compare this model with two other (shape-preserving) situations concerning four walkers, namely a square in two dimensions (system S) and a tetrahedron moving in three dimensions (system T), both moving through reflections (flips). In each case we first investigate the CM's motion by means of numerical simulations. Using algebraic WTDs we find that in all three cases the CMs move diffusively at short and long times, with a subdiffusive cross-over region in between. We stress that various statistical effects, such as the subdiffusive cross-over region, occur even for a small number of involved random walkers if only the WTD is broad [19]. We provide analytical approximations for the short- and long-time diffusion coefficients. By comparing two different systems (S and Q) in two dimensions it turns out that pinning (the pausing of one random walker for a long time) is a fundamental feature in the determination of the long-time diffusion coefficient. A comparison of the two-dimensional versus three-dimensional motion shows that the temporal aspects (i.e. the WTD) are decisive, whereas the spatial aspects are less important.

2. The models

As mentioned, we shall study the motion of four random walkers under holonomic constraints in two and three dimensions. We start with system Q, where each of the four random walkers is placed on the edges of a square lattice of unit length, $a_Q = 1$. Q describes a polymer ring and moves through kink–jumps. We display the situation in figure 1(a), where we denote the random walkers by 1, 2, 3 and 4 and start from a square configuration. As a first possible move, walker 1 moves to 3 (this is the only possibility for 1 to move). Afterwards 1 as well as 3 are solely able to return to 1's former location. Random walkers 2 and 4 may jump by flipping around their opposite sides. Figure 1(a) also shows some of the places which may be visited by Q's CM in the course of time.

The second system S is a square, whose shape stays unchanged during its motion. We envisage the random walkers involved to be placed at the centre of S's four sides. Making the dumbbell parallel, S moves by flips, i.e. reflections of S with respect to its sides, see figure 1(b), where walker 3 stays fixed, while walkers 1, 2, 3 and 4 move to mirrored positions; we associate this flip with walker 1. At each flip S's CM moves over a distance equal to the square's lateral length $a_S = 1$. In figure 1(b) we show a series of S's jumps, starting with a jump of 1 followed by jumps of 2 and 3. The possible positions of the CM form a square lattice.

As a third case we analyse a tetrahedron T, which moves in three dimensions. The random walkers sit at T's vertices and the motion again involves reflections: each walker jumps by being reflected with respect to the plane spanned by the other three vertices, see figure 1(c). Note that T extends the dumbbell (one dimension) and the triangle (two dimensions) models to three dimensions, and that, analogously to S, stays form invariant during the motion. A few of T's jumps and the complex way T's CM move are shown in figure 1(c). Again T's lateral length a_T is taken to be 1.

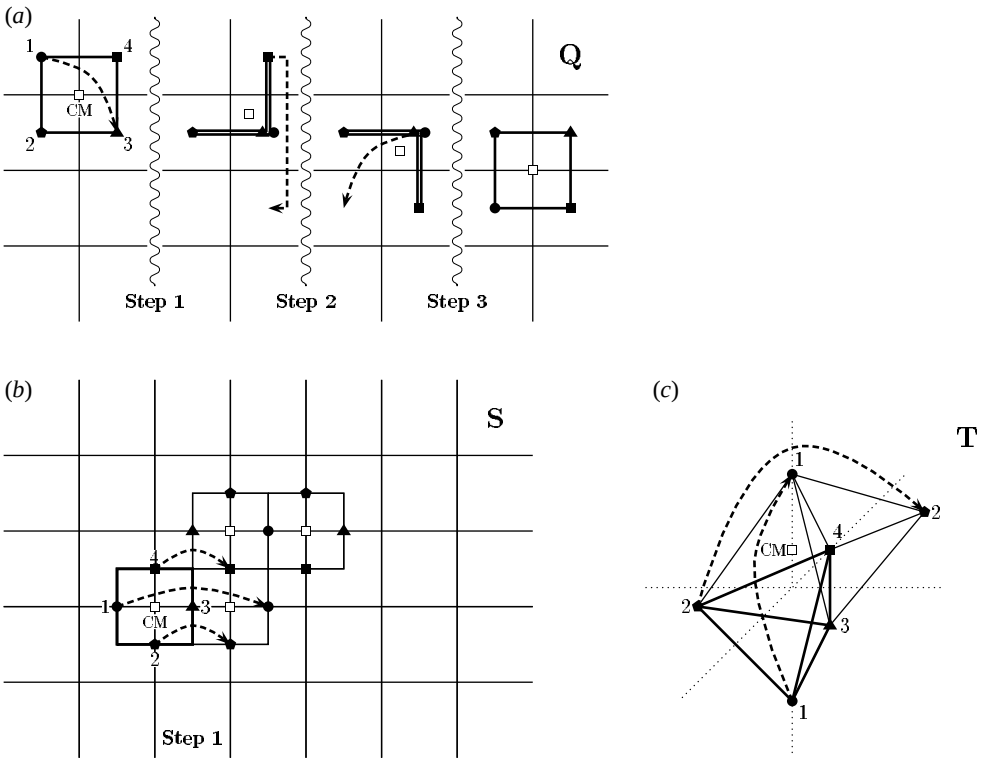

Figure 1. (*a*) A series of displacements of Q, which start with random walker 1, followed by moves of 4 and 1. The squares indicate positions which can be visited by Q's CM. (*b*) A series of displacements of configuration S. Note that S's CM performs a random walk on a square lattice. (*c*) Two displacements of T.

We now turn to the temporal development of the motion, and assume that all jumps (flips) involved follow a preassigned WTD, which gives the waiting time between two consecutive steps of the same random walker. Each of the four random walker follows its own internal clock: because of the constraints, however, the overall motion of the systems (S, Q or T) is quite complex, even when the internal clocks are uncorrelated and the WTD is the same for all walkers. Moreover, for the renewal process connected with $\Psi(t)$ two situations may be distinguished [9, 10].

(1) The first event takes place at $t = 0$. The WTD for the subsequent jumps is $\Psi(t)$. Such renewal processes are called *ordinary* (ORP).

(2) The WTD $\Psi_0(t)$ for the first event differs from $\Psi(t)$, the WTD for all following events. The renewal process is now called *delayed*.

If $\mu = \int_0^\infty \Psi(t)\,\mathrm{d}t < \infty$, processes which started a long time ago are in equilibrium; for such *equilibrium* renewal processes (ERP) one has

$$\Psi_0(t) = \frac{1}{\mu}[1 - F(t)] \tag{1}$$

with $F(t) = \int_0^t \Psi(s)\,\mathrm{d}s$. It can be shown [10] that only for ERPs the average value $N(t)$ of the number of renewals $n(t)$ in the time interval $(0, t)$ equals

$$N(t) = \langle n(t) \rangle = \frac{t}{\mu} \tag{2}$$

and that the forward WTD $H(t,\xi)$, which is the propability that the first renewal epoch following epoch t lies within $(t, t+\xi)$, is given by

$$H(t,\xi) = \frac{1}{\mu}\int_0^{\xi}[1-F(s)]\,\mathrm{d}s = \int_0^{\xi}\Psi_0(s)\,\mathrm{d}s \tag{3}$$

i.e. is independent of t. For ORPs, equations (2) and (3) are only valid in the limit of large t [10]. We will mainly focus on the following WTD [1, 2, 19]:

$$\Psi(t) = \frac{\gamma}{(1+t)^{\gamma+1}} \qquad \text{with } \gamma > 1. \tag{4}$$

This function shows an algebraical behaviour, $\Psi \simeq \gamma/t^{\gamma+1}$ for large t, and is well behaved, with $\mu < \infty$, for all t.

3. Numerical simulations

We used the WTD equation (4) to numerically determine the motion of the CM for all three models (S, Q and T) considered. We performed simulations for a wide range of γ-values and proceeded as follows. First we fixed the value of γ in equation (4); then we listed for each realization of the motion the times at which each walker jumps by using $\Psi_0(t)$ and $\Psi(t)$ for ERP and of $\Psi(t)$ for ORP. In this way we obtained four distinct lists for the four walkers involved. Next, we ordered all jumps into a cumulative list in ascending temporal order and moved the random walkers according to this list. By storing the time and the CM's coordinates after each jump we obtained CM's trajectory. For every model and each choice of the WTD (ERP or ORP, and value of γ) we generated 10^4 trajectories, in order to obtain reasonably good statistics.

Figure 2 shows simulation results for Q, where the motion starts from a square configuration, see figure 1(a) where CM's mean square displacement $\langle R^2(t)\rangle$ is plotted as a function of time, both for ORP and ERP. Evidently $\langle R^2(t)\rangle$ is diffusive at short and long times, paralleling the results of [1, 2, 19]. These two limiting, diffusive regions are

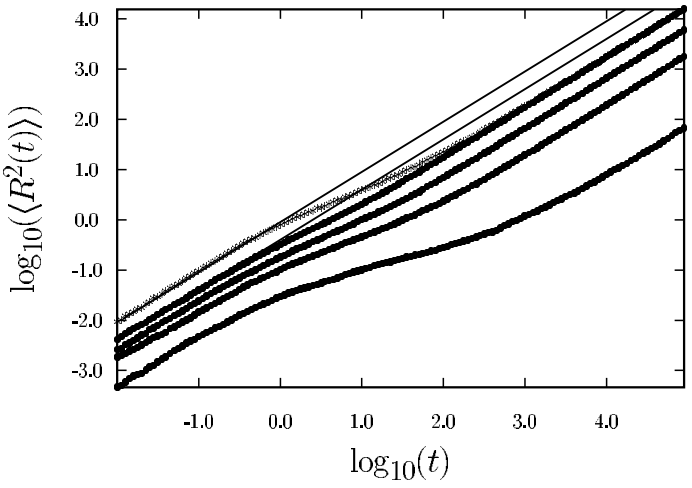

Figure 2. $\langle R^2(t)\rangle$ for Q's CM for $\gamma = 1.8$, 1.5, 1.3 and 1.1 (from top to bottom) for an ERP. The first two curves are simulation results for ORP ($*$) and ERP ($\bullet$), which coincide at long times. The light curves approximate CM's short-time behaviour for $\gamma = 1.8$, equation (8), see text for details.

connected by a subdiffusive regime when the difference between the short- and the long-time diffusion constants is large. Note that Q's overall motion resembles that of a polymer ring. This, as in the case of [19], where large chains ($N = 50$) were considered, leads to a subdiffusive behaviour, reminiscent of Rouse-type motion and of reptation [20, 21]. In our model, however, as in [19], the interaction between the surroundings and Q is wholly described by the WTD, and the subdiffusive cross-over behaviour results from the WTD's algebraic form; exponential WTDs lead to a simple diffusion of the CM [1].

Note that in figure 2 the scales are logarithmic and the different dynamical regimes may stretch over several orders of magnitude in time. The $\langle R^2(t)\rangle$ values for S's and T's CM show a similar behaviour.

To understand the behaviour we note first that according to [9] the Laplace transform of the average number $N(t)$ of renewals in $(0, t)$ is

$$N^*(s) = \frac{\Psi_1^*(s)}{s[1 - \Psi^*(s)]} \tag{5}$$

where $\Psi_1(t) = \Psi(t)$ for ORPs and $\Psi_1(t) = \Psi_0(t)$ for ERPs. For short times $\Psi_1(t) \approx \Psi_1(0)$. With this approximation equation (5) reads for $s \to \infty$

$$N^*(s) \approx \frac{\Psi_1(0)}{s^2} \tag{6}$$

and hence, for small t

$$N(t) = \langle n(t)\rangle \approx \Psi_1(0)t. \tag{7}$$

For ERPs equation (7) equals equation (2), since $\Psi_1(0) = \Psi_0(0) = 1/\mu$, see equation (1). Now as long as $N(t) \leqslant 1$ holds, one is at the stage of the first jump of a walker. Using equation (7) the CM's mean square displacement for short times is

$$\langle R^2(t)\rangle = 4b^2\Psi_1(0)t \tag{8}$$

where b^2 is the mean square displacement of the CM per jump. It is immediate to verify that for the first jump (where Q starts from a square configuration) $b_S^2 = a_S^2$, $b_Q^2 = 1/8a_Q^2$ and $b_T^2 = 1/6a_T^2$ hold. Figure 2 shows exemplarily for $\gamma = 1.8$ that equation (8) approximates Q's CM mean square displacement at short times well both for ORP and ERP. The same holds for the other values of γ which we considered ($\gamma = 1.5$, 1.3 and 1.1) and also for the systems S and T. For large t the behaviour of $\langle R^2(t)\rangle$ is again diffusive, but the corresponding diffusion constant is smaller than the value which follows from equation (8). We now turn to the discussion of this long-time behaviour.

4. The long-time diffusion constant

To understand the long-time behaviour we have to take into account the interplay between the temporal aspect of the motion (WTD) and the holonomic constraints. Note that series of jumps involving the same walker are very common when γ is small; however, if a walker moves twice in succession each of the models considered (S, Q and T) returns to its initial position without any change in the CM's position. The same is true for the series of jumps involving several walkers; as long as not all walkers move, the systems are (*vide infra* for a discussion of subtleties) in general, confined to a limited region in space. The basic idea is hence that of pinning [1, 2], i.e. the fact that the long-time diffusion constant vanishes when at least one walker does not move from its initial position. To account for pinning we follow [2] and denote by effective steps the minimal sequences in a fixed, preassigned series of jumps which start, say, with a jump of random walker 1 and end just before a

jump of 1, such that between these two events 2, 3 and 4 have each performed at least one jump. The effective steps cover the set of jumps completely, so that each jump belongs to exactly one effective step. Two examples for effective steps may be 122234333241 and 11111233311141. The end of an effective step is the starting point of the next one. If correlations between effective steps are disregarded, the long-time diffusion constant is given by [2]:

$$D = \frac{c^2}{\langle T \rangle} \tag{9}$$

where c^2 is the mean square displacement of the CM per effective step and $\langle T \rangle$ its mean duration. Since

$$\langle T \rangle = \frac{t}{\langle n_s(t) \rangle} \tag{10}$$

one now needs to evaluate $\langle n_s(t) \rangle$, the overall mean number of effective steps for a given set of jumps. An exact, analytical expression for $\langle n_s(t) \rangle$ is hard to obtain; what is now helpful is the fact that according to [2] the following inequalities hold:

$$\langle n_r(t) \rangle \leqslant \langle n_s(t) \rangle \leqslant (N-1)\langle n_r(t) \rangle \tag{11}$$

where N is the number of involved random walkers (here $N = 4$) and $\langle n_r(t) \rangle$ is the mean number of returns of, say, walker 1. A return of 1 occurs if between two consecutive jumps of 1 jumps of all three other random walkers take place. Inequalities (11) result from the fact that each return of 1 corresponds to an effective step of the overall process (the reverse is, in general, not true) and that the end of each effective step lies either within a return of 2, of 3 or of 4. Now $\langle n_r(t) \rangle$ equals $p\langle n(t) \rangle$, with p being the probability that an arbitrary jump of 1 is the starting point of a return [2]. Since we have $H(t, \xi) = H(\xi)$ for ERPs, p is given by

$$p = \int_0^\infty \mathrm{d}\xi \; \Psi(\xi) H(\xi)^3 = \frac{6(\gamma-1)^3}{(2\gamma-1)(3\gamma-2)(4\gamma-3)}. \tag{12}$$

Equation (12) makes it possible to estimate D,

$$\frac{6c^2(\gamma-1)^4}{(2\gamma-1)(3\gamma-2)(4\gamma-3)} \leqslant D \leqslant \frac{18c^2(\gamma-1)^4}{(2\gamma-1)(3\gamma-2)(4\gamma-3)}. \tag{13}$$

By considering CM's possible displacements after one effective step and determing the largest one we find that $\max\{c_Q^2\} = \frac{65}{8}a_Q^2 = 8.125a_Q^2$ and $\max\{c_T^2\} = \frac{29\,200}{6561}a_T^2 \simeq 4.451a_T^2$. We can thus bound c^2 in equation (13) from above and have (for Q and T) as an approximation for D

$$D = k\frac{6(\gamma-1)^4}{(2\gamma-1)(3\gamma-2)(4\gamma-3)} \tag{14}$$

where k is left to be a fitting parameter (the case S requires a more detailed discussion, *vide infra*). In figure 3 we have plotted the results of D found from numerical simulations for all three models in a wide range of γ-parameters. For Q and T the plotted results are practically indistinguishable. A least squares fit to the data, using equation (14) leads to $k_Q = 2.655 \pm 0.07$ and $k_T = 2.625 \pm 0.03$. In figure 3 we plot equation (14) using $k = 2.6$; this choice turns out to be very good in the range $1.1 \leqslant \gamma \leqslant 10$, as can be seen by inspection. We conclude that the structure of equation (14) is, indeed, correct. Note that the equation contains both the spatial restrictions (form of the expression) as well as the influence of the WTD $\Psi(t)$ (value of γ).

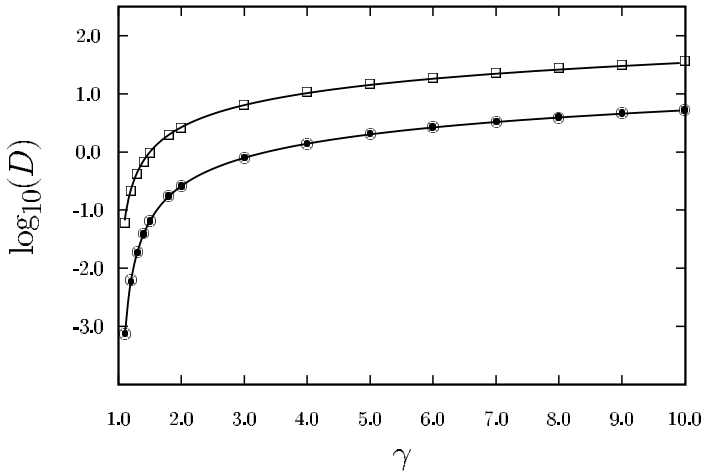

Figure 3. Long-time diffusion constant D for S (□), Q (⊗) and T (●) as a function of γ. The full curves represent equation (14) for $k = 2.6$ (lower curve) and equation (17) (upper curve).

Astonishingly at first, from figure 3 it turns out that S moves faster than Q and T and that the γ-dependence of D differs from equation (14), a fact which becomes especially clear at values of γ close to unity. The reason for these findings can be understood when realizing that S's CM motion decouples in the x- and y-direction. Note that jumps of S related to, say, 2 and 4 force 1 and 3 to follow, see figure 1(b). In the configuration S walker 1 can hence move even when we do not relate a jump to it; here pinning of a walker and no jumps related to it are two different concepts. It follows that equations (13) and (14) are not suitable to describe S's long-time diffusion constant.

A careful analysis shows that S moves like a dumbbell both in the x- and y-direction. For a dumbbell, considering the two-walkers motion leads to [1]:

$$\langle n_s(t)\rangle = \langle n_r(t)\rangle. \tag{15}$$

This, paralleling the expressions above, results for a dumbbell in:

$$D = k\frac{(\gamma-1)^2}{2\gamma-1} \tag{16}$$

with $k \simeq 4$ [1]. We expect for S therefore:

$$\langle R^2(t)\rangle = \langle R_x^2(t) + R_y^2(t)\rangle = 2Dt = 8\frac{(\gamma-1)^2}{2\gamma-1}. \tag{17}$$

In figure 3 we have also plotted equation (17); the result is in very good agreement with our numerical simulations, as can be seen by inspection.

As a final note we remark that the expressions for D at long times, equations (14) and (16), depend on powers of $(\gamma - 1)$. Hence, the closer γ approaches unity, the larger the subdiffusive, cross-over region. On the other hand, for $\gamma \gg 1$, the CM's motion is nearly diffusive at all times.

5. Conclusions

In this paper we have studied the motion of three different arrangements, each involving four random walkers, which are coupled through holonomic constraints. The random

walkers jump according to algebraic WTDs. The CM's mean square displacement behaves diffusively both at short and long times, with a subdiffusive crossover region in between. Interestingly, the constraints lead to qualitatively different long-time behaviours, depending on whether decoupling of the motion occurs (as for S) or not (as for Q and T). This effect is fundamental, whereas the question of dimensionality (Q moves in two dimensions, T moves in three dimensions) is secondary.

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